

Effect of TiO₂ and V₂O₅ Additives on Chemical Mullite

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Abstract

The effect of titanium dioxide and vanadium pentaoxide additive on the formation and mechanical properties of chemical mullite from aluminosilicate diphasic gel was compared. The diphasic gel precursor was synthesized by sol-gel route using inorganic salts. The microstructure and phase analysis of the sintered masses from the gel precursors were carried out by means of SEM and XRD studies. It has been observed that both the additives improved the mechanical properties of the mullite ceramics.

Key Words

Chemical Mullite; Sol-Gel; Additives; Diphasic Gel; Microstructure

Introduction

Mullite is basically a non-stoichiometric compound with molecular formula $Al_2[Al_{2+2x}Si_{2-2x}O_{10-x}]$, where x denotes the missing oxygen atoms per unit cell, (0.17 - 0.59) [Cameron WE, 1977]. The important engineering properties of mullite include, low thermal expansion and thermal conductivity, good thermal and chemical stability, high melting point, low creep rate etc and therefore, mullite is widely used in the production of heat resistant material [Schneider, H et al, 1990; Hynes, AP et al, 1991; Belogurova, OA et al, 2009], electronic packaging [Ramakrishnan, V et al, 1992] thin film, window material for the mid-infrared wavelength range from 3 to 5 μm [Aksay, A et al, 1991] etc. Mullite synthesized by chemical process like sol-gel is termed as chemical mullite [Schneider, H et al, 1994]. Depending on short range atomic arrangement, gel can be classified into two categories, namely, monophasic and diphasic gel. In the diphasic gel system the heat of reaction of the different phases or presumably the heat of mixing in an amorphous system provides an extra energy for the densification process [Wei, W et al, 1998].

Mullite can incorporate different metal oxide into its structure in different amounts. The importance of preparation methods for both pure and doped mullite has increased significantly in recent times. Naga et al showed that increasing TiO₂ content increased the bending strength of the mullite bodies prepared through sol-gel process. Sola et al. observed that increment in titania concentration reduced the crystallization temperature of single phase mullite gel. Hong et al. showed that titania doping can reduce the glass viscosity, the sintering temperature and the onset temperature for anisotropic grain growth. Roy et al. observed that addition of V₂O₅ can improve the crystallite size of mullite.

In the present investigation effect of 3% (w/w) of TiO₂ and V₂O₅ on the crystallization of mullite from Al₂O₃-SiO₂ diphasic gel was compared by analyzing the microstructure and mechanical properties of sintered products.

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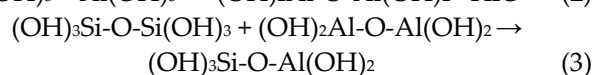
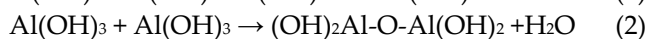
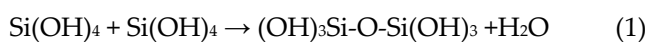
Experimental

The diphasic mullite gel was synthesized by using analar grade of aluminum nitrate nonahydrate (ANN) and liquid sodium silicate (sp. Gr. 1.6 and molar ratio of Na₂O: SiO₂ =1:3). Silicic acid was prepared from sodium silicate by ion exchange process. Silicic acid and ANN solution were mixed together and ammonia solution (1:1) was added to it until pH~9. The gel formed was filtered, washed and dried at 80°C. The dried gel was then subjected to chemical analysis; measurement of surface area and bulk density (Table-1). The gel was mixed thoroughly with 3% (w/w) TiO₂ and V₂O₅ (reagent grade) followed by compaction at 100 MPa and sintering at 1400, 1500 and 1600°C

respectively with 2 hours of soaking. The sintered masses were characterized by XRD analysis using Rigaku X-ray diffractometer with Cu target (Miniflex, Japan) and SEM investigation by FEI Quanta microscope (US). Following BS 1902 Part 1A, 1966 specification, the apparent porosity, bulk density and flexural strength of the samples were measured.

Results and Discussion

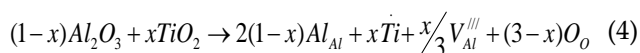
The aluminosilicate hydrogel was formed by colloidal interaction of silicic acid and aluminum hydroxide. FTIR spectral analysis didn't show any significant band for Si-O-Al linkage which confirmed the diphasic nature of the gel. So aluminosilicate gel is formed as a result of following condensation reaction:



The synthesized gel had very low bulk density (0.27g/cm^3) and a considerably high surface area ($70\text{m}^2/\text{gm}$) indicating its considerable high surface activity of the samples. Calcination of the gel was performed to prevent excessive shrinkage due to the loss of water and other volatiles during the final stage of sintering. Initial concentration of alumina was kept slightly higher to minimize the formation of silica bearing glassy phase after sintering.

Mullite formation in diphasic aluminosilicate gel system is controlled by dissolution precipitation reactions [Bartsch M et al, 1999]. For nucleation and subsequent growth of mullite crystal, the dissolution velocity of Al_2O_3 into the SiO_2 liquid is important.

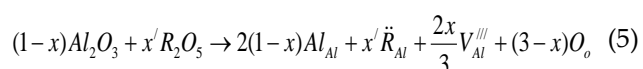
With TiO_2 additive, tetrahedrally coordinated Ti^{4+} substituted Al^{3+} in mullite lattice structure



Where 'V' is vacancy and 'x' is the atomic fraction of Al substitution by Ti.

This substitution of Al^{3+} by Ti^{4+} is possible because the ionic radii of Al^{3+} (53.5 pm) is lower than that of Ti^{4+} (56 pm) in tetrahedral coordination.

With V_2O_5 doping, the substitution of aluminum by vanadium in the octahedral site is almost similar:



Where R indicates vanadium ion, 'V' is vacancy and 'x' is the atomic fraction of Al substitution by V.

During heat treatment of V_2O_5 , the cation V (+5) may be converted to its lower oxidation states V (+4) and V (3+). In all these oxidation states vanadium is in octahedral co-ordination and ionic radii of these cations are higher than that of Al^{3+} . V_2O_5 addition is advantageous compared to TiO_2 due to its (V_2O_5) low melting point (690°C). So at lower temperature, a liquid phase is developed which can reduce the mullitization temperature considerably by minimizing the viscosity of the SiO_2 -rich liquid phase.

In the XRD diagram of the TiO_2 doped samples (Figures 1B) significant amount of aluminum titanate phase was observed at 1500°C . On increasing temperature aluminum titanate can undergo decomposition liberating incipiently formed active aluminum consuming further silica with the formation of more mullite. From the XRD pattern of the V_2O_5 doped samples (Figures 1C) it was observed that the amount of mullite phase substantially increased with the additives and the sintering temperature. Presence of small amount of aluminum vanadium oxide was observed in the diffractogram.

In presence of both the additives the %d-error values for mullite phase decreases as the sintering temperatures increases suggesting that increase in the sintering temperature enhanced the crystallization of mullite. In presence of TiO_2 , the lattice structure expanded by almost 1.85% whereas in presence of V_2O_5 the expansion was negligible. The average sizes of the mullite crystallites at different sintering temperatures were also determined from Scherrer's equation (Table-2). At higher sintering temperature the matrix had a more constraining effect on the growth of mullite crystal in case of TiO_2 addition. With increase in sintering temperature, the size of the crystallite decreased with TiO_2 but with V_2O_5 it increased.

TiO_2 and V_2O_5 exhibited positive influence on the densification of the mullite ceramics (Fig. 3 and 4). With TiO_2 additive the decomposition of the formed Al_2TiO_5 phase at higher sintering temperature affected the densification of mullite and consequently on apparent porosity values of the samples. With V_2O_5 additive some liquid phases was formed with SiO_2 at higher temperature thereby promoting densification in the samples.

The flexural strength of the sintered samples improved significantly with the addition of TiO_2 and V_2O_5 additive to the aluminosilicate gel samples (Fig 5& Fig 6). From the SEM photomicrograph (Fig 2A, 2B and 2C)

of the sintered samples; it was observed that the grains were properly interlocked in the presence of both TiO_2 and V_2O_5 additives. In both the cases presence of the devitrified and highly viscous phase at the grain boundaries resulted in the minimization of the grain boundary sliding due to fracture stress. The rate of improvement of flexural strength was the maximum at the sintering temperature of 1500°C and its reduced rate of improvement at 1600°C was related to the formation of more liquid phases.

Conclusion

Chemical mullite was prepared from diphasic gel. The gel was synthesized by the colloidal interaction of silicic acid and $\text{Al}(\text{NO}_3)_3$ solution. TiO_2 and V_2O_5 were used as sintering additive separately for the processing of mullite ceramics. The sintering behavior of mullite was promoted in presence of both the additives. The mechanical properties of the sintered masses were also improved significantly due to improved microstructure and favorable phase compositions.

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TABLE-1: PHYSICOCHEMICAL PROPERTIES OF THE HYDROGEL

Properties	Value
$\text{SiO}_2(\text{wt}\%)$	17.86
$\text{Al}_2\text{O}_3(\text{wt}\%)$	48.23
Ignition Loss (wt%)	33.91
Bulk Density (g/cm^3)	0.27
Sp. Surface Area (m^2/g)	70

TABLE-2: CHANGE IN CRYSTALLITE SIZE AT DIFFERENT SINTERING TEMPERATURE

Firing Temperature ($^\circ\text{C}$)	TiO_2 doped Mullite (nm)	V_2O_5 doped Mullite (nm)
1400	30.29	24.77
1500	26.18	26.18
1600	24.78	30.29

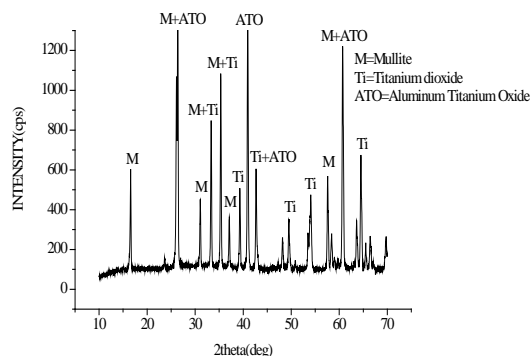


FIG-1A: XRD DIAGRAM OF 3% TiO_2 DOPED ALUMINOSILICATE GEL SINTERED AT 1600°C

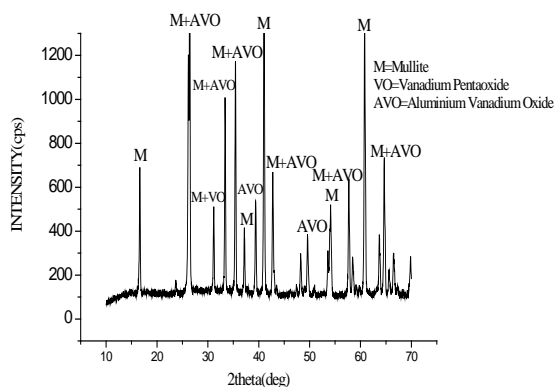


FIG-1B: XRD DIAGRAM OF THE ALUMINOSILICATE GEL WITH 3% V_2O_5 ADDITIVE SINTERED AT 1600°C

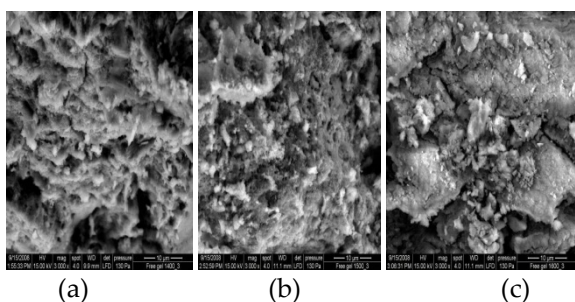


FIG-2A: SCANNING ELECTRON MICROGRAPH OF THE ALUMINOSILICATE GEL SAMPLES (NO ADDITIVE)

(a) sintered at 1400°C (b) sintered at 1500°C (c) sintered at 1600°C

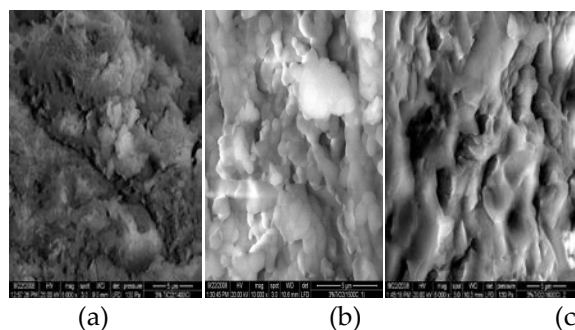


FIG-2B: SCANNING ELECTRON MICROGRAPH OF THE 3% TiO_2 DOPED ALUMINOSILICATE GEL

(a) sintered at 1400°C (b) sintered at 1500°C (c) sintered at 1600°C

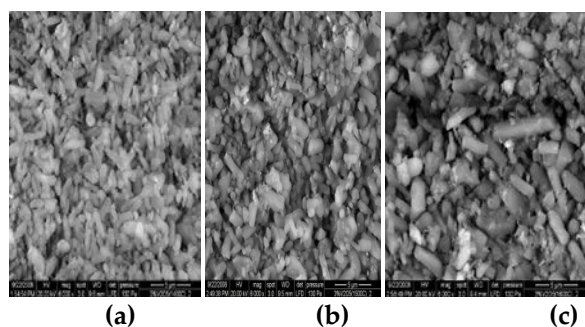


FIG-2C: SCANNING ELECTRON MICROGRAPH OF THE ALUMINOSILICATE GEL WITH 3% V_2O_5 DOPED

(a) sintered at 1400°C (b) sintered at 1500°C (c) sintered at 1600°C

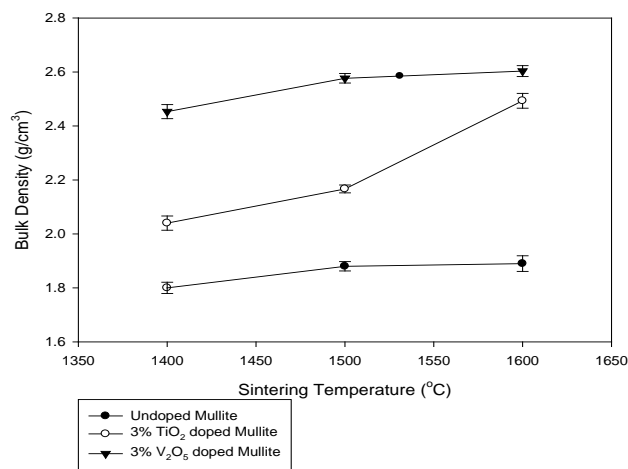


FIG-3 VARIATION IN BULK DENSITY WITH SINTERING TEMPERATURE

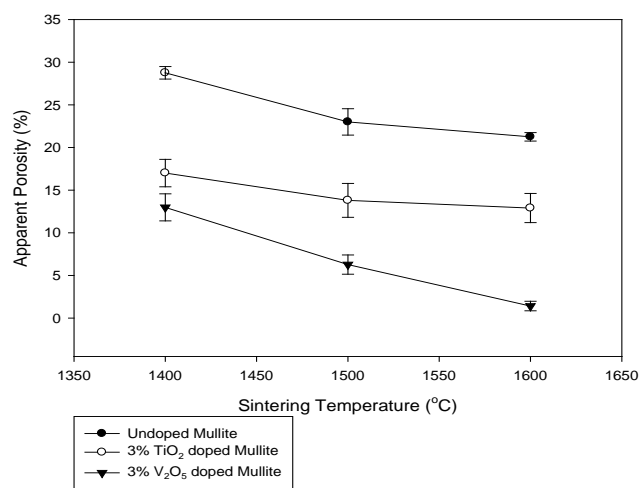


FIG-4 VARIATION IN APPARENT POROSITY WITH SINTERING TEMPERATURE

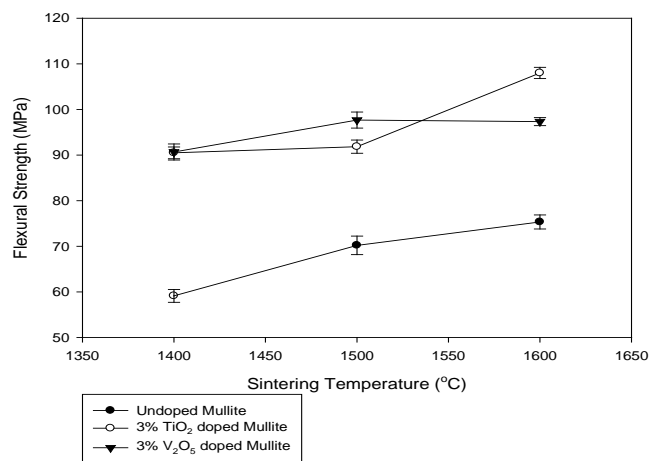


FIG5 VARIATION IN FLEXURAL STRENGTH WITH SINTERING TEMPERATURE